Viscoelastic Behavior of Polymers

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The behavior of complex fluids, such as polymer blends and multiblock copolymers (e.g., Estane®) is intermediate between that of solids and fluids. For short times, the response is elastic and the stress is proportional to the applied strain. On the other hand, for late times a fluid-like response with stress proportional to the strain rate is typically observed. The effect of viscoelasticity on polymer morphology becomes even more important as the "dynamical asymmetry" between the polymer components increases. The behavior of the "slow" and "fast" components leads to deformation and phase separation properties that are quite unlike those observed for symmetric systems.

The "two-fluid" model, in which separate velocities are needed for the monomeric components to describe viscous drag effects and the viscoelastic nature of the polymeric chains, has been reasonably successful in understanding blends and homopolymers. However, a phenomenological Ginzburg-Landau free energy is used to describe the composition or density of the chains. In contrast, we have developed a scheme that couples the chemical potentials from a Self-Consistent Mean Field Method (SCFT) within the framework of a two-fluid model so that the polymeric nature of the fluids is taken into account, albeit within a mean field approximation that is good for dense systems or melts. This Hydrodynamic Self-Consistent Field Theory (HSCFT) extends the SCFT technique to nonequilibrium regimes, retaining its thermodynamic detail while accessing experimentally relevant timescales. An advantage of this approach is that is it easily extensible to systems of arbitrary complexity for which it is difficult to construct a Ginzburg-Landau free energy.

Many of the mesoscale properties of the system relax on timescales shorter than thermodynamic timescales and are effectively in local equilibrium on hydrodynamic timescales, which allows us to employ SCFT techniques to calculate their properties. The hydrodynamic model thus simulates the large-scale convective and diffusive flows, as well as the polymer's viscoelastic behavior. By employing parallelized pseudo-spectral techniques, we are able to model relatively large systems in three dimensions with high accuracy and long time-scales.

The HSCFT approach provides a new tool that can be employed to perform numerical experiments on a wide range of complex polymer systems under various processing conditions. Although our code is currently limited to modeling the properties of diblocks in the low shear linear viscoelastic regime, with a reasonable effort it can easily be extended to more complex systems such as linear multiblocks copolymers and star and branched copolymers. Additionally, the system can be extended to include particles of arbitrary shape and size using compatible phase-field techniques. One example of interest might be a system of polymers mixed with carbon nano-tubes. Some progress has also been made toward modeling systems with complex wall geometries to capture the behavior of polymers in thin films or in the presence of microfluidic channels.

Figure 1 shows a diblock copolymer system that has been rapidly quenched from its homogenous well-mixed phase into a microphase-separated region. The blue and yellow in the cross-section are the two monomer components and the interior shows the yellow matrix of one component that is embedded in the other component. In Fig. 2, we can see that the early stages of phase separation are dominated by purely diffusive effects. However, at later times cooperative convective flows contribute in a nontrivial way. The free energy as a function of time shows a significant drop coincident with the phase-ordering process that takes place over the diffusive time scale. Further decrease in the free energy is accompanied by rearrangement of larger scale motions due to convection, which occurs on a second, much longer timescale.

Figure 2—
Diffusive velocity (w) and convective velocity (v) vs time.

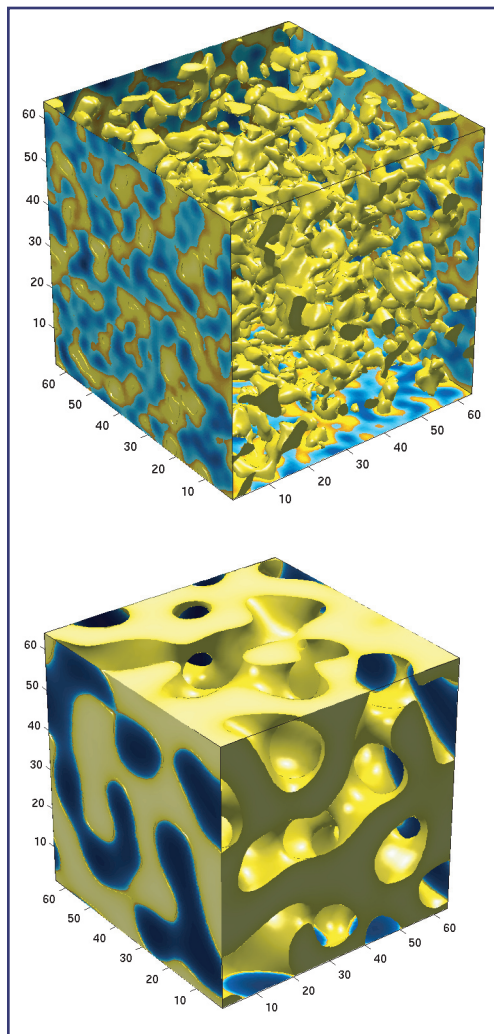

Figure 3—
Helmholtz free energy vs time.

Figure 1—
Early and intermediate stages of microphase separation in a diblock copolymer melt. The yellow and blue zones represent areas of high concentration of the two dissimilar monomers. In the interior, one monomer species is removed to reveal the complex defect-filled morphologi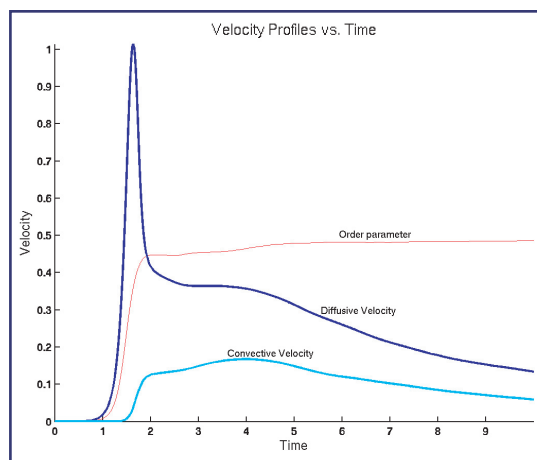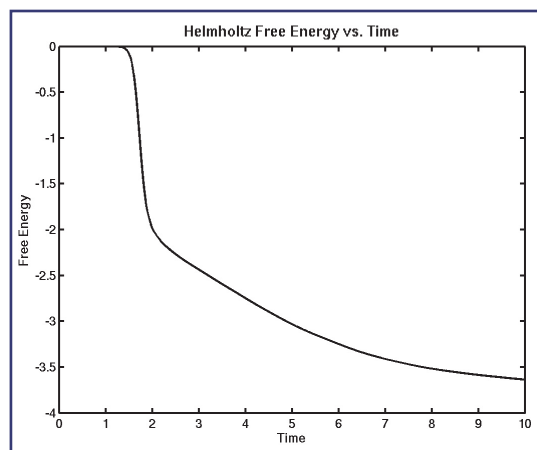es that are typical of these materials.